Colloids and Surfaces A: Physicochem. Eng. Aspects 509 (2016) 158–165

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Different ionic liquid modified hypercrosslinked polystyrene resin for purification of catechins from aqueous solution

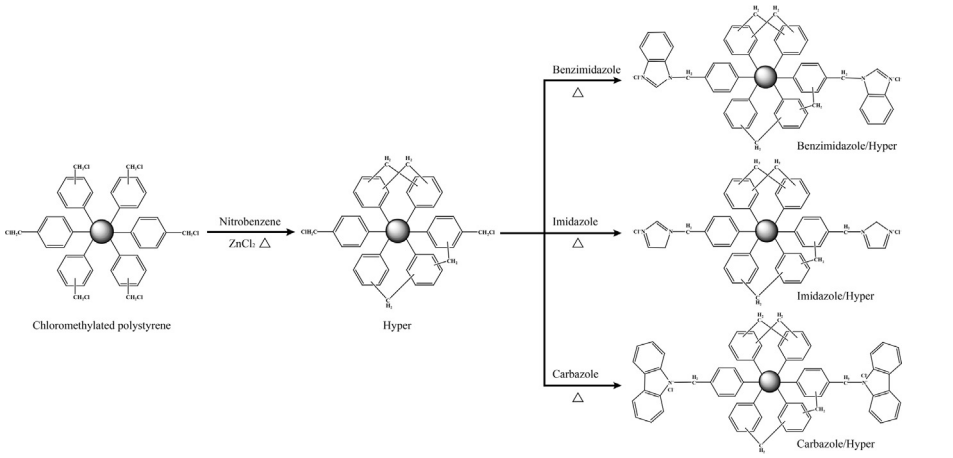
Dong Pei[a,b], Xiaoyu Wu[a,c], Yi Liu[a,b], Ting Huo[a], Duolong Di[a,b,*], Mei Guo[c], Lei Zhao[c], Bingpeng Wang[c]

[a] Key Laboratory of Chemistry of Northwestern Plant Resources and Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China
[b] Centre of Resource Chemical and New Material, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Qingdao 266100, People's Republic of China
[c] Key Laboratory of Chemistry and Quality for Traditional Chinese Medicines of the College of Gansu Province, Gansu University of Chinese Medicine, Lanzhou 730000, People's Republic of China

HIGHLIGHTS

- Different ionic liquid modified hypercrosslinked polystyrene resins were synthesized.
- Equilibria and kinetics characterized by common models.
- The adsorption mechanism mainly ascribed to the synergistic effect.
- The steric hindrance of ionic liquid functional group in the hypercrosslinked resins was a crucial factor.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 June 2016
Accepted 27 August 2016
Available online 28 August 2016

Keywords:
Hypercrosslinked
Ionic liquid
Adsorption mechanism
Catechin

ABSTRACT

A series of different ionic liquid modified hypercrosslinked polystyrene resins were prepared and evaluated for their adsorption properties where benzimidazole modified hypercrosslinked polystyrene resins exhibited best selectivity against catechins comparison with others ionic liquid modified hypercrosslinked resins and commercial resins. The maximum adsorption capacity of Benzimidazole/Hyper are up to 75.3 mg/g for (−)-epigallocatechin gallate and 101.7 mg/g for (−)-epicatechin. The pseudo-second-order kinetic equation and intra-particle diffusion model could describe the entire adsorption process of (−)-epigallocatechin gallate and (−)-epicatechin onto ionic liquid modified hypercrosslinked resins. Isothermal equilibrium curves showed a good fitness with the Langmuir and Freundlich models.

* Corresponding author at: Key Laboratory of Chemistry of Northwestern Plant Resources and Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China.
E-mail address: didl@licp.cas.cn (D. Di).

http://dx.doi.org/10.1016/j.colsurfa.2016.08.071

Evaluated thermodynamic parameters revealed that adsorption was spontaneous and endothermic. The results from the sequential adsorption-desorption cycles showed that Benzimidazole/Hyper resins held good desorption and reusability. The adsorption mechanism was indicated to be the synergistic effect of molecular sieving effect, multiple adsorption interactions and specific surface area. In addition, the steric hindrance of ionic liquid functional group in the hypercrosslinked polymeric resins was a crucial factor for the order of the adsorption capacity.

1. Introduction

Tea is one of the most consumed flavored functional beverages in the world. A plentiful of scientific data has shown that the beneficial health effects of tea are mainly ascribed to its polyphenolic compounds [1]. Catechins are the most abundant components in tea polyphenol, comprising (−)-epigallocatechin gallate (EGCG), (−)-epicatechin (EC), (−)-epicatechin gallate (ECG), (−)-epigallocatechin (EGC) and so on. Among these catechins, EGCG accounts for more than 50% of the total catechin content in tea [2]. EGCG has proven to exhibit various pharmacological effects, like possessing antioxidant activity and antimicrobial activities, reduction in cancer mortality, protection from Parkinson's disease and Alzheimer's disease, reducing the risk of cardiovascular diseases, suppression of inflammatory conditions [3–8]. Consequently, separation and purification of EGCG have been significantly challenging in chemistry.

Various methods and technologies for EGCG separation from tea have been investigated [9–14]. Among the effective methods and technologies is adsorption by reason of simplicity, economy, high efficiency, and environment-friendly behavior [15]. A large number of literatures focus on the adsorption materials for separation of EGCG [16–18]. In our previous study, commercially available AB-8 resins are modified with ionic liquids via the Friedel–Crafts reaction. In between AB-8 resins and Ionic liquid/MAR, the adsorption capacity of EGCG and EC onto Ionic liquid/MAR only increased by 10% [19,20]. Analysis of the reason considers that the contribution of introduced functional group on the resins is really limited. The specific surface area may be the driving forces of adsorption. Later, ionic liquid modified hypercrosslinked polystyrene resins are synthesized, which possess high specific surface area, bimodal distribution of pore sizes and ionic liquid functional group [21]. The EGCG and EC uptakes on ionic liquid modified hypercrosslinked polystyrene resins (HP-IL16) are remarkably larger than other resins. Compared with that of macroporous adsorption resins Seplite D101, the uptake of EGCG was enhanced by 31%, whereas the uptake of EC was enhanced by 88%. Analysis of the adsorption mechanism suggest that the synergistic effect of the specific surface area, molecular sieving effect, and multiple adsorption interactions play a predominant role in the adsorption process [22]. However, the EGCG and EC uptakes on HP-IL16 have a certain distance from fractional adsorption materials, such as amino-functionalized ordered mesoporous silica SBA-15 [14].

In order to develop high adsorption capacity and suitable for large-scale industrial application adsorbents for separation of EGCG, we synthesized a series of different ionic liquid-modified hypercrosslinked polystyreneresins to increases the adsorption capacity by interacting with EGCG and EC via multiple interactions. The purpose of this work is that structure-function relationship has been systemically studied between different ionic liquid-modified hypercrosslinked polystyrene resins and EGCG and EC.

2. Materials and methods

2.1. Materials

Low crosslinked chloromethylated polystyrene (Chloromethylated PS) was from Xi'an Sunresin Technology Co., Ltd. (Shaanxi,China), its crosslinking degree was 6%, chlorine content was measured to be 17.0%. Imidazole, benzimidazole, carbazole, nitrobenzene, *N,N*-dimethylformamide, sodium hydroxide, anhydrous zinc chloride, acetone, hydrochloric acid, and ethanol was bought from Tianjin Chemical Reagent Co., Inc. (Tianjin, China) with analytical reagent grade. Purified deionized water was laboratory-prepared. HPLC-grade methanol was purchased from Shandong Yuwang Industrial Co., Ltd. (Shandong, China). Standard EGCG and EC were supplied by Chengdu preferred Biological Technology Co., Ltd. (Sichuan, China) with purity of 98.0%.

2.2. Synthesis of the polymeric adsorbents

The synthesis routes to the different ionic liquid-modified hypercrosslinked polystyrene resins are outlined in Scheme 1. The synthesis was similar to the previous work. In a typical procedure, a solution of nitrobenzene was added Chloromethylated PS resins. The resulting system was swollen overnight. 4 g of anhydrous zinc chloride was added into the reaction flask at 323 K with mild mechanical stirring. The reaction mixture was evenly heated to 388 K within 1 h and carried out continuously at 388 K for 10 h. The resins was washed with acetone, 1% hydrochloric acid (v/v), and de-ionized water until neutral; extracted with ethanol in Soxhlet apparatus for 12 h; and then dried at 323 K in vacuum. The hypercrosslinked polystyrene resin, Hyper, was obtained.

10 g of the Hyper beads was swollen in 135 mL of *N,N*-dimethylformamide for 12 h. 2 g of sodium hydroxide and 1.6 g of imidazole were added into the flask. After being stirred for about 12 h at 343 K, the polymeric beads were rinsed with distilled water, extracted with ethanol for 12 h, and dried at 323 K in vacuum. The imidazole-modified hypercrosslinked polystyrene resins, Imidazole/Hyper, was synthesized.

Benzimidazole/Hyper and Carbazole/Hyper were prepared in almost the same procedure as for Imidazole/Hyper.

2.3. Characterization of the resins

Chlorine content determination was determined by the Volhard method [23]. Elemental analysis of polymeric resins was obtained with Vario EL elemental analysis system. The pore structure of polymeric resins was performed at a Micromeritics ASAP 2020 automatic surface area by nitrogen adsorption and desorption at 77 K. FT-IR spectra were collected with a Nexus 870 FT-IR spectrometer in the 400–4000 cm^{-1} region (KBr pressed disks). Scanning electron microscopy (SEM) experiments were carried out by a JSM–6701 scanning electron microscope.